

EP 0 675 209 A1



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



⑪ Publication number:

0 675 209 A1

⑫

## EUROPEAN PATENT APPLICATION

⑬ Application number: 95104333.0

⑮ Int. Cl. 8: C22C 21/00, C22C 45/08,  
C22F 1/04, C22C 1/04

⑯ Date of filing: 23.03.95

⑭ Priority: 29.03.94 JP 59145/94

Sendai-shi,

Miyagi (JP)

Inventor: Inoue, Akihisa

11-806, Kawauchi-jutaku,

Mubanchi,

Kawauchi

Aoba-ku,

Sendai-shi,

Miyagi (JP)

Inventor: Kimura, Hisamichi

44, Azatobeihashi,

Arahama,

Watari-cho

Watari-gun,

Miyagi (JP)

Inventor: Shinohara, Yoshiyuki

c/o Teikoku Piston Ring Co., Ltd.,

1-9-9, Yaesu

Chou-ku,

Tokyo (JP)

Inventor: Horio, Yuma, c/o Yamaha

Corporation

10-1, Nakazawa-cho

Hamamatsu-shi,

Shizuoka (JP)

Inventor: Kita, Kazuhiko

3-18-8, Yagiyamaminami,

Talhaku-ku

Sendai-shi,

Miyagi (JP)

⑯ Designated Contracting States:

DE FR GB

⑰ Applicant: YKK CORPORATION

No. 1, Kanda Izumi-cho

Chiyoda-ku,

Tokyo (JP)

Applicant: Masumoto, Tsuyoshi

3-8-22, Kamisugi

Aoba-ku

Sendai-shi

Miyagi (JP)

Applicant: Inoue, Akihisa

11-806, Kawauchi-jutaku,

Mubanchi,

Kawauchi,

Aoba-ku

Sendai-shi,

Miyagi-ken (JP)

Applicant: TEIKOKU PISTON RING CO. LTD.

9-9, Yaesu 1-chome

Chuo-ku

Tokyo (JP)

Applicant: YAMAHA CORPORATION

10-1, Nakazawa-cho

Hamamatsu-shi

Shizuoka-ken (JP)

⑯ Inventor: Masumoto, Tsuyoshi

3-8-22, Kamisugi,

Aoba-ku

⑯ Representative: Patentanwälte Leinweber &

Zimmermann

Rosental 7/II Aufg.

D-80331 München (DE)

⑯ High strength aluminum-based alloy.

⑯ A high strength aluminum-based alloy, which having a composition of the general formula:  $Al_{1-a}Q_aM_bX_cT_d$ , wherein Q represents at least one element selected from the group consisting of Mn, Cr, V, Mo and W; M represents at least one element selected from the group consisting of Co, Ni, Cu and Fe; X represents at least one element selected from rare earth elements including Y or Mm; T represents at least one element selected from the group consisting of Ti, Zr and Hf; and  $a$ ,  $b$ ,  $c$  and  $d$  represent the following atomic percentages:  $1 \leq a \leq 7$ ,

**EP 0 675 209 A1**

$0 < b \leq 5$ ,  $0 < c \leq 5$  and  $0 < d \leq 2$ , and contains quasi-crystals in the structure thereof. The alloy of the present invention is excellent in the hardness and strength at both room temperature and a high temperature, and also in thermal resistance and ductility. In addition, it is usable as a high specific strength material having a high strength and a low specific gravity due to a small amount of addition of rare earth element or elements.

BACKGROUND OF THE INVENTION

1 Field of the Invention

5 The present invention relates to an aluminum-based alloy having excellent mechanical properties such as a high hardness and a high strength.

2. Description of the Prior Art

10 An aluminum-based alloy having a high strength and a thermal resistance has hitherto been produced by a rapid-solidification technique such as a liquid quenching method. Particularly, an aluminum-based alloy produced by the rapid solidification technique as disclosed in Japanese Patent Laid-Open No. 275732/1989 is amorphous or microcrystalline. In particular, the microcrystalline alloy disclosed therein is in the form of a composite composed of a solid solution of an aluminum matrix, a microcrystalline aluminum matrix phase 15 and a stable or metastable intermetallic compound phase.

However, although the aluminum-based alloy disclosed in the above-mentioned Japanese Patent Laid-Open No. 275732/1989 is an excellent alloy having a high strength, a high thermal resistance, a high corrosion resistance and an excellent workability as a high-strength material, its excellent characteristic properties as the rapidly solidifying material are impaired in a high-temperature range of 300 °C or above, 20 and thus its thermal resistance, particularly, strength at a high temperature, has room for further improvement.

In addition, it is relatively difficult to improve the specific strength of the alloy disclosed in the above-mentioned Japanese Patent Laid-Open No. 275732/1989, since such an alloy contains an element having a relatively high specific gravity. Thus, a further improvement in or relating to the specific strength and 25 ductility of the alloy is expected.

SUMMARY OF THE INVENTION

Therefore, the object of the present invention is to provide an aluminum-based alloy having an excellent 30 thermal resistance, high strength at room temperature, high strength and hardness at a high temperature, excellent ductility and high specific strength by forming an aluminum-based alloy having such a structure that at least quasi-crystals are finely dispersed in an aluminum matrix.

The above-described problem can be solved by the present invention which provides a high strength aluminum-based alloy having a composition of the general formula:



wherein Q represents at least one element selected from the group consisting of Mn, Cr, V, Mo and W; M represents at least one element selected from the group consisting of Co, Ni, Cu and Fe; X represents at 40 least one element selected from rare earth elements including Y or misch metal; T represents at least one element selected from the group consisting of Ti, Zr and Hf; and a, b, c and d represent the following atomic percentages:  $1 \leq a \leq 7$ ,  $0 < b \leq 5$ ,  $0 < c \leq 5$  and  $0 < d \leq 2$ , and containing quasi-crystals in the structure thereof.

The quasi-crystals are in an icosahedral phase (I phase), decagonal phase (D phase) or similar crystal 45 phase.

The structure of the aluminum-based alloy is composed of a quasi-crystal phase and any one phase of an amorphous phase, aluminum or a supersaturated solid solution of aluminum. The latter can be a composite (mixed phase) of an amorphous phase, aluminum and supersaturated solid solution of aluminum. The structure may contain an intermetallic compound formed from aluminum and other elements and/or 50 intermetallic compounds formed from the other elements in some cases. The presence of the intermetallic compound is particularly effective in reinforcing the matrix or controlling the crystal grains.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

55 The aluminum-based alloy of the present invention can be directly produced from a molten alloy having the above-described composition by a single-roller melting-spinning method, a twin-roller melting-spinning method, an in-rotating-water melt-spinning method, various atomizing methods, a liquid quenching method such as a spray method, a sputtering method, a mechanical alloying method, a mechanical grinding method

or the like. The cooling rate which varies a little depending on the composition of the alloy is usually about  $10^2$  to  $10^4$  K/sec in such a method.

In the aluminum-based alloy of the present invention, the quasi-crystals can precipitate from the solid solution of the aluminim-based alloy of the present invention by heat-treating the rapidly solidified material obtained by the above-described method or by a thermal processing, for example, by compacting the rapidly solidified material and extruding the resultant compact. The temperature in this step is particularly preferably 360 to 600 °C.

The detailed description will be made on the reasons for the limitation in the present invention.

A reason for limiting the atomic percentages in the above-mentioned general formula to 1 to 7% of  $a$ , 5% or below (excluding 0%) of  $b$ , 5% or below (excluding 0%) of  $c$  and 2% or below (excluding 0%) of  $d$  is that when the atomic percentages are in these ranges, the strength of the alloy is higher than that of an ordinary high-strength aluminum alloy available on the market while the high ductility is kept even at room temperature or 300 °C or higher. Particularly preferred range is:  $3 \leq (a+b+c+d) \leq 7$ .

The element  $Q$  which is at least one element selected from the group consisting of Mn, Cr, V, Mo and  $W$  is indispensable for the formation of the quasi-crystals. By combining the element  $Q$  with an element  $M$  which will be described below, the formation of the quasi-crystals is facilitated and the thermal stability of the alloy structure can be improved.

$M$  represents at least one element selected from the group consisting of Co, Ni, Cu and Fe. By combining the element  $M$  with the element  $Q$  described above, the formation of the quasi-crystals is facilitated and the thermal stability of the alloy structure can be improved as in the case of  $Q$  element. The element  $M$  has only a low dispersibility in the main element Al; it is effective in reinforcing the Al matrix; and it forms various intermetallic compounds with the main element Al or other elements to contribute to the improvement in the strength and thermal stability of the alloy.

The element  $X$  is at least one element selected from rare earth elements including Y or misch metal (Mm). Such elements are effective in enlarging the quasi-crystal phase-forming zone into a low solute concentration area of the added transition metal and also in improving the refining effect by cooling the alloy. Thus, the element  $X$  is effective in improving the mechanical properties and ductility of the alloy by the improvement in the refining effect.

The element  $T$  is an element having a low dispersibility in the main element Al. It is effective in refining Al and also in improving the ductility of the alloy without impairing the mechanical strength and thermal resistance.

The amount of the quasi-crystals in the above-described alloy structure is preferably 20 to 70% by volume. When it is below 20% by volume, the object of the present invention cannot be sufficiently attained and, on the contrary, when it exceeds 70% by volume, the alloy will become brittle and, therefore, the obtained material might not be sufficiently processed. The amount of the quasi-crystals in the alloy structure is still preferably 50 to 70% by volume.

The average grain size in the aluminum phase or supersaturated aluminum solid solution phase is preferably 40 to 2,000 nm. When the average grain size is below 40 nm, the resultant alloy has an insufficient ductility, though its strength and hardness are high. When it exceeds 2,000 nm, the strength is rapidly reduced to make the production of the high strength alloy impossible.

The average grain size of the quasi-crystals and various intermetallic compounds which are contained if necessary is preferably 10 to 1,000 nm. When the average grain size is below 10 nm, they difficultly contribute to the improvement in the strength of the alloy and when such fine grains are present in an excess amount in the structure, a brittleness of the alloy might be caused. On the contrary, when it exceeds, 1,000 nm, the grains are too large to maintain the strength and the possibility of losing its reinforcing function is increased.

Thus, by restricting the composition to that shown by the above-mentioned general formula, the Young's modulus, strength at high temperature and room temperature, fatigue strength and so on can be further improved.

The alloy structure, quasi-crystals, grain size in each phase, dispersion state and so on of the aluminum-based alloy of the present invention can be controlled by suitably selecting the production conditions. Thus, by controlling these conditions, the alloy having desired properties such as strength, hardness, ductility and thermal resistance can be produced depending on the purpose.

Further, properties required of an excellent superplastic material can be imparted by controlling the average grain size in the aluminum phase or supersaturated aluminum solid solution phase in the range of 40 to 2,000 nm and the average grain size of the quasi-crystals or various intermetallic compounds in the range of 10 to 1,000 nm as described above.

The following Examples will further illustrate the present invention.

EP 0 675 209 A1

Example 1

An aluminum-based alloy powder having each composition given in Table 1 was prepared with a gas atomizer. The aluminum-based alloy powder thus prepared was packed into a metallic capsule and then 5 degassed to obtain an extrusion billet. The billet was extruded with an extruder at a temperature of 360 to 600 °C. The mechanical properties at room temperature (hardness and strength at room temperature), mechanical properties at a high temperature (strength after keeping at 300 °C for 1 hour) and ductility of the extruded material (consolidated material) obtained under the above-described production conditions were examined to obtain the results given in Table 2.

10

Table 1

15	Inventive sample No.	Composition (at. %)					
		Al	Q	X	M	T	
	1	balance	Mn = 1.0		Y = 1.5	Co = 3.0	Ti = 0.5
	2	balance	Mn = 1.5		Ce = 2.0	Co = 2.5	Ti = 1.0
	3	balance	Mn = 2.0		Gd = 1.0	Fe = 4.0	Ti = 1.5
20	4	balance	Mn = 2.5		Mm = 1.0	Fe = 1.0	Ti = 2.0
	5	balance	Mn = 3.0		Mm = 1.0	Ni = 1.0	Zr = 0.5
	6	balance	Mn = 3.5		La = 1.0	Ni = 2.0	Zr = 1.0
	7	balance	Mn = 4.0		Nd = 0.5	Fe = 1.0	Zr = 1.5
	8	balance	Mn = 5.0		Y = 2.0	Cu = 2.5	Zr = 2.0
25	9	balance	Mn = 6.0		Ce = 1.5	Co = 1.5	Hf = 0.5
	10	balance	Cr = 1.0		Mm = 2.5	Co = 2.0	Hf = 1.0
	11	balance	Cr = 1.5		La = 1.5	Fe = 1.0	Ti = 0.5
	12	balance	Cr = 2.0		Mm = 1.0	Ni = 2.0	Ti = 1.0
	13	balance	Cr = 3.0		Y = 1.0	Co = 1.0	Ti = 1.0
30	14	balance	Cr = 3.5		Ce = 1.0	Fe = 3.0	Ti = 1.5
	15	balance	Cr = 4.0		Y = 3.5	Ni = 3.0	Ti = 2.0
	16	balance	Cr = 5.0		Mm = 2.0	Cu = 2.0	Ti = 1.5
	17	balance	Mn = 1.0	Cr = 0.5	Mm = 1.0	Co = 2.0	Zr = 0.5
	18	balance	Mn = 1.5	Cr = 0.5	Gd = 1.2	Fe = 1.0	Zr = 1.0
35	19	balance	Mn = 2.0	Cr = 1.0	La = 1.0	Co = 2.0	Zr = 1.5
	20	balance	Mn = 0.5	Cr = 1.5	Ce = 0.5	Fe = 1.0	Hf = 1.0
	21	balance	V = 1.0		Ce = 1.0	Co = 2.5	Ti = 0.5
	22	balance	V = 1.5		Y = 1.0	Fe = 2.0	Zr = 1.0
	23	balance	V = 3.0		Ce = 1.0	Co = 1.0	Ti = 1.0
40	24	balance	Mo = 2.0		La = 1.0	Ni = 1.0	Ti = 1.0
	25	balance	Mo = 2.0		Ce = 0.5	Co = 1.5	Zr = 1.0
	26	balance	W = 1.0		Mm = 0.5	Co = 3.0	Ti = 1.0
	27	balance	W = 1.0		Mm = 1.0	Fe = 2.5	Zr = 0.5
	28	balance	W = 1.5		Ce = 0.5	Co = 1.5	Hf = 0.5

45

50

55

Table 2

Inventive sample No.	Tensile strength (MPa)	Tensile strength 300 °C(MPa)	Hardness (Hv)	Elongation (%)
1	870	325	290	16
2	810	320	292	22
3	880	340	298	18
4	960	335	320	15
5	890	321	288	21
6	820	335	295	19
7	850	341	280	18
8	920	345	295	16
9	940	350	297	16
10	1020	355	315	17
11	980	341	321	18
12	1030	339	295	17
13	990	345	295	16
14	890	348	285	18
15	980	336	292	20
16	930	339	288	21
17	920	348	286	18
18	920	345	297	17
19	920	341	285	19
20	930	339	275	18
21	770	305	280	16.2
22	870	325	288	15.2
23	920	330	330	17.0
24	920	300	290	16.0
25	970	310	310	17.0
26	930	320	298	13.3
27	970	335	310	14.0
28	980	315	315	12.7

It is apparent from the results given in Table 2 that the alloy (consolidated material) of the present invention has excellent hardness and strength at room temperature and also excellent strength and ductility at a high temperature (300 °C). Also, it was found that although in the production of the consolidated materials, the alloys were subjected to heating, a change in the characteristic properties of the alloy by heating was only slight and the difference in the strength between room temperature and high temperature was also only slight. These facts indicate that the alloy has an excellent thermal stability.

The extruded material obtained under the above-described production conditions was cut to obtain TEM (transmission electron microscope) observation test pieces. The structure of the alloy and the grain size in each phase were observed. The results of the TEM observation indicated that the quasi-crystals formed an icosahedral phase (I phase) singly or a mixed phase comprising the icosahedral phase and a decagonal phase (D phase). A similar crystal phase was recognized depending on the kind of the alloy. The amount of the quasi-crystals in the structure was 20 to 70% by volume.

The alloy structure was a mixed phase of aluminum or supersaturated aluminum solid solution phase and the quasi-crystal phase. Depending on the kind of the alloy, various intermetallic compound phases were also found. The average grain size in aluminum or supersaturated aluminum solid solution phase is 40 to 2,000 nm. The average grain size in the quasi-crystal phase or intermetallic compound phase was 10 to 1,000 nm. In the composition wherein intermetallic compounds were precipitated, the intermetallic compounds were uniformly and finely dispersed in the alloy structure.

In the Examples of the present invention, the alloy structure and the particle size in each phase were controlled by the degassing (including the compaction during the degassing and heat processing in the extrusion step).

As described above, the alloy of the present invention is excellent in the hardness and strength at both room temperature and a high temperature, and also in thermal resistance and ductility. In addition, it is usable as a high specific strength material having a high strength and a low specific gravity due to a small

amount of addition of rare earth element or elements.

Since the alloy has a high thermal resistance, the excellent characteristic properties obtained by the rapid solidification method and the characteristic properties obtained by the heat treatment or thermal processing can be maintained even when a thermal influence is exerted thereon in the course of the processing.

In the present invention, the aluminum-based alloy having a high strength and thermal resistance can be provided because of the special crystal structure thereof, which contains a specified amount of the quasi-crystal phase having a high thermal resistance and hardness.

10 **Claims**

1. A high strength aluminum-based alloy having a composition of the general formula:



wherein Q represents at least one element selected from the group consisting of Mn, Cr, V, Mo and W; M represents at least one element selected from the group consisting of Co, Ni, Cu and Fe; X represents at least one element selected from rare earth elements including Y or misch metal; T represents at least one element selected from the group consisting of Ti, Zr and Hf; and a, b c and d represent the following atomic percentages:  $1 \leq a \leq 7$ ,  $0 < b \leq 5$ ,  $0 < c \leq 5$ , and  $0 < d \leq 2$ , and containing quasi-crystals in the structure thereof.

2. A high strength aluminum-based alloy according to Claim 1, which satisfies:  $3 \leq (a + b + c + d) \leq 7$ .

25 3. A high strength aluminum-based alloy according to Claim 1 or 2, which has an elongation of at least 10%.

4. A high strength aluminum-based alloy according to any of Claims 1 to 3, wherein the quasi-crystals are in an icosahedral phase (I phase), decagonal phase (D phase) or similar crystal phase.

30 5. A high strength aluminum-based alloy according to any of Claims 1 to 4, wherein the amount of the quasi-crystals contained in the structure is 20 to 70% by volume.

6. A high strength aluminum-based alloy according to any of Claims 1 to 5, wherein the structure is composed of a quasi-crystal phase and any one of an amorphous phase, aluminum and a super-saturated solid solution of aluminum.

35 7. A high strength aluminum-based alloy according to Claim 6, which further contains various intermetallic compounds formed from aluminum and other elements and/or intermetallic compounds formed from other elements.

40 8. A high strength aluminum-based alloy according to any of Claims 1 to 7, which is any of a rapidly solidified material, a heat-treated material obtained by heat-treating the rapidly solidified material, and a compacted and consolidated material obtained by compacting and consolidating the rapidly solidified material.



European Patent  
Office

EUROPEAN SEARCH REPORT

Application Number  
EP 95 10 4333

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP-A-0 561 375 (MASUMOTO ET AL.) 22 September 1993 *Examples, Table 1 and claims* ---	1,2,4-8	C22C21/00 C22C45/08 C22F1/04 C22C1/04
X	EP-A-0 534 470 (MASUMOTO ET AL.) 31 March 1993 *Table 4, Sample No.s 9,23 and claims* ---	1-8	
X	EP-A-0 475 101 (YOSHIDA KOGYO K.K.) 18 March 1992 *Table 1, Sample No.4 and claims* ---	1,4-8	
X	JOURNAL OF NON-CRYSTALLINE SOLIDS, vol. 153&154, no. 2, February 1993 US, pages 86-91, SINGH,A AND RANGANATHAN,S. 'Quasicrystalline and crystalline phases and their twins in rapidly solidified Al-Mn-Fe alloys' *Figure 3, discussion and conclusion* ---	1,4,6,7	
A	MATERIALS SCIENCE FORUM, vol. 150-151, 1994 CH, pages 15-34, STEURER,W. 'The structure of quasicrystals' *Pages 20-22, 25* ---	1-8	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C22C C22F
A	PHILOSOPHICAL MAGAZINE A, vol. 69, no. 1, January 1994 pages 45-55, KIM,D.H. AND CANTOR,B. 'Quasicrystalline and related crystalline phases in rapidly solidified Al-Fe alloys' *Page 49 53,54* ---	1-8	
A	EP-A-0 587 186 (YOSHIDA KOGYO CO. LTD.) 16 March 1994 ---	1-8 -/-	
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
MUNICH	21 June 1995	Badcock, G	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 95 10 4333

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.)
A	EP-A-0 445 684 (YOSHIDA KOGYO K.K.) 11 September 1991 *Page 3 and claims* -----	1-8	
			TECHNICAL FIELDS SEARCHED (Int.Cl.)
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
MUNICH	21 June 1995	Badcock, G	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			